

FREE RADICAL CRACKING OF HIGH MOLECULAR WEIGHT BRANCHED ALKANES

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Studies of thermocracking of branched alkanes play an important role in several areas, including high temperature catalytic cracking, delayed coking, manufacture of olefins, degradation of polymers, and geochemistry. Although principal chemical reactions involved in thermocracking under relatively mild conditions are well known (1-4), detailed information about cracking of large branched molecules is lacking from the literature, mostly because of analytical problems - identification of reaction products, various branched alkanes and olefins, in the carbon atom number range $C_8 - C_{20+}$.

This paper discusses principal reaction stages of thermocracking of pristane, phytane, and squalane in the liquid state under mild conditions ($250^{\circ}C$, 24 h) and presents analysis of reactivities of various C-H bonds in the hydrogen abstraction reactions as well as reactivities of various C-C bonds in the β -scission reactions.

EXPERIMENTAL PART

Thermocracking of pristane, phytane, and squalane at $250-300^{\circ}C$ for 24 h in the liquid state was carried out in small glass ampoules sealed under vacuum. Under these conditions the reaction yields equimolar mixtures of isoalkanes and olefins with branched chains. Addition of a mineral clay (bentonite) to the ampoules results in conversion of the olefins into a complex mixture of various secondary products while keeping the alkanes formed in the cracking reaction intact. Comparison of the gas chromatograms of the cracking products obtained with and without the clay assists in identification of branched alkanes.

A Hewlett-Packard 5880A gas chromatograph equipped with the flame ionization detector, operated in the split injection mode with a split ratio 100:1, was used to obtain chromatographic data. The column used was a 50 m, 0.02 mm i.d., fused silica capillary coated with 0.50 micron film of cross-linked methyl silicone. Helium carrier gas was used at a flow of 1 ml/min. The column oven temperature was programmed from $40^{\circ}C$ to $300^{\circ}C$ at $5^{\circ}C/min$ and held at $300^{\circ}C$ until complete elution of a sample. Sample size was 1.0 microliter. Detector and injector temperatures were held at $325^{\circ}C$. Samples were diluted with CS_2 before injection.

The techniques used for assignment of alkane and olefin peaks in gas chromatograms of the thermocracked products are discussed elsewhere (5, 6). They were based on the application of a modified additivity principle (7) which allows quantitative estimation of peak positions of complex molecules (multibranched alkanes and olefins) from the data on peak positions of more simply built molecules (monobranched alkanes, linear olefins).

A generally used procedure of presentation of retention times for peaks of hydrocarbons in gas chromatograms is calculation of their Kovats factors (KF) from their retention times RT (8).

$$KF(\text{iso-alkane } C_nH_{2n+2}) = 100(n-1) +$$

$$100[RT(\text{iso-alkane}) - RT(n-C_{n-1}H_{2n})] / [RT(n-C_nH_{2n+2}) - RT(n-C_{n-1}H_{2n})] \quad 1)$$

For example, the peak of an iso-alkane situated in the middle between peaks of $n-C_{12}H_{26}$ and $n-C_{13}H_{28}$ has KF 1250. We found it more convenient to use a different parameter for the purpose - a relative retention factor, RRF (5, 6):

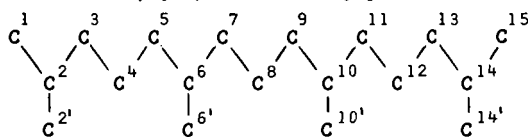
$$RRF = [KF(\text{iso-alkane } C_nH_{2n+2}) - KF(n\text{-alkane } C_nH_{2n+2})] / 100 \quad 2)$$

This factor is a negative number representing a normalized relative precedence of the peak of a hydrocarbon with respect to the peak of the normal alkane with the same carbon atom number.

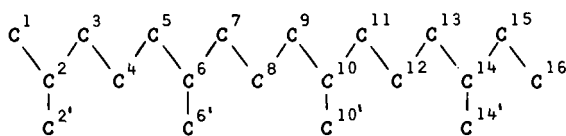
RESULTS AND DISCUSSION

Numbering of carbon atoms in the skeletons of the three isoprenoid molecules follows:

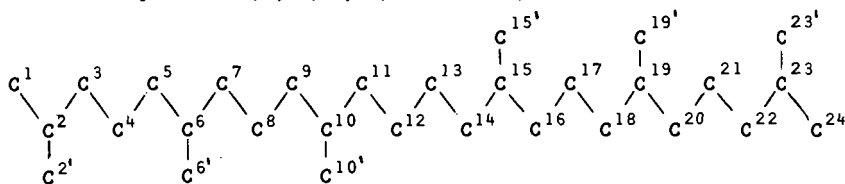
Pristane (2,6,10,14-tetramethylpentadecane)



Phytane (2,6,10,14-tetramethylhexadecane)

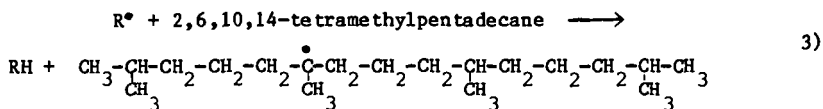


Squalane (2,6,10,15,19,23-hexamethyltetracosane)

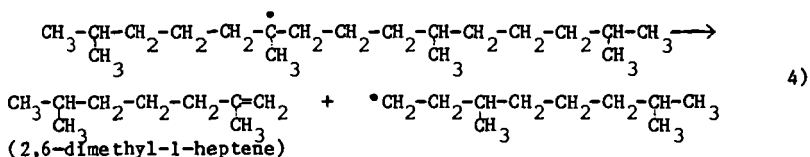


Conversions in the thermocracking reactions (250°C, 24 h) were: for pristane - 6.0%, for phytane - 2.7%, for squalane - 6.4%. Under these mild conditions only three stages of the radical chain reactions should be considered: formation of a parent radical, fission of the radical with the formation of an olefin and a smaller alkyl radical, and the chain transfer reaction yielding a low molecular weight alkane. One example of these three reactions involving a radical attack on the sixth position of the pristane molecule and the β -scission of the C_7-C_8 bond is:

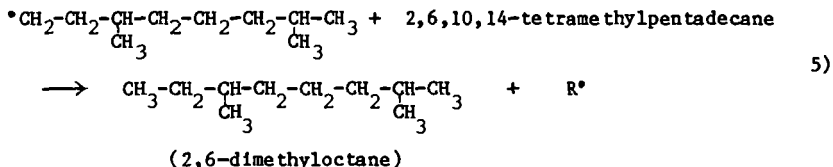
Formation of a parent radical (hydrogen abstraction reaction):



β -scission reaction:



Chain transfer reaction:



Reactions 3 and 5 are, in a general sense, the same reaction of hydrogen abstraction and they are separated here to emphasize chemistry of the reaction product formation. It is generally accepted (2, 4) that radical reactions of alkanes at low temperatures in the liquid state are accompanied by intramolecular radical isomerization (hydrogen atom shifts via five- and six-atom cyclic transition states) and by intermolecular hydrogen exchange reactions (reverse of reaction 3 with RH being the substrate molecule). The joint result of these two processes is the equilibrium distribution of primary radicals in terms of radical site positions, with the equilibrium being governed by relative radical stabilities.

Tables 1 and 2 list all possible alkanes and olefins which are formed in the principal thermocracking reactions of pristane, phytane, and squalane, experimental and calculated RRF values for the alkanes and olefins, and positions of radical attacks resulting in the formation of corresponding hydrocarbons. Peak areas for the products were used as the basis for the evaluation of reactivities of various bonds in two reactions - hydrogen abstraction (Reaction 3) and β -scission (Reaction 4).

β -scission reactions

In the majority of cases several β -scission reactions are possible for a radical formed in Reaction 3 (except for radicals in positions 2 in all isoprenoids and in position 16 for phytane). Analysis of reaction products allows estimation of probabilities of the scission reactions.

Tertiary radicals. Tertiary radicals in positions 6 and 10 are situated in very symmetrical environments. As a consequence,

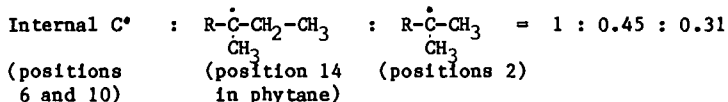
probabilities of β -scissions for the adjacent bonds are virtually equal. The ratios of products formed in the C_4-C_5 and C_7-C_8 bond scissions (radicals in position 6) are in the range 1.06-0.98 for all isoprenoids. The same ratios (1.08-0.99) were found for C_8-C_9 and $C_{11}-C_{12}$ bond scissions in phytane and squalane (radicals in position 10). On the other hand, the probability of the CH_2-CH_2 bond ($C_{12}-C_{13}$) scission in the phytane radical (in position 14) is 10.6 times higher than that for the CH_2-CH_3 bond ($C_{15}-C_{16}$) which corresponds to the ΔE_{act} difference, ca. 2.5 kcal/mol.

Secondary radicals. Similarly to the previous case, if a secondary radical is situated in a symmetrical environment (positions 8 in all molecules, position 12 in phytane) the probability of the two β -scissions are identical (with precision ca. 4%) according to expectations. However even a slight deviation from the symmetry, in positions 4, results in a deviation from the equality. The ratio between the probabilities for the scission of C_2-C_3 and C_5-C_6 bonds is ca. 0.63. When secondary radicals are in positions 7 (or positions 9 in phytane and squalane) the scission involves different chemical bonds. In these cases the ratios of the scission rates for the CH_2-CH_2 bonds (C_8-C_9 for radicals in positions 7) and for the CH_2-CH bonds (C_5-C_6) are ca. 0.71 (+7%). The same ratio (scission of $C_{12}-C_{13}$ vs. C_9-C_{10}) for the phytane radical in position 11 is 0.58. However, the $C_{12}-C_{13}$ bond in squalane is ca. 10% more reactive in β -scission than the C_9-C_{10} bond. Data for the pristane radical (in position 5) provide the most complete information of the relative probabilities of β -scission reactions. The ratios of the reactions for the CH_2-CH_2 bond (C_8-C_9), the CH_2-CH bond (C_5-C_6), and the CH_3-CH bond (C_6-C_6') are 4.72 : 6.70 : 1.

Reactivities of C-H bonds in hydrogen abstraction reactions

Tertiary C-H bonds

Tertiary C-H bonds are the most active in radical hydrogen abstraction reactions as emphasized by their low bond energies, ca. 90 kcal/mol (2, 4). Our data show that reactivities of the C-H bonds in 6 and 10 positions are equal for all three isoprenoids (corresponding product yields are in the range 1.00-1.03). The ratios of products formed from the end- and internal tertiary radicals are:



If one takes into account different scission patterns for these radicals (discussed earlier) and the existence of only one β -scission route for the end-tertiary radicals these ratios translate into the ratios of formation rates for corresponding radicals ca. 1 : 0.7 : 0.8.

Secondary radicals

The isoprenoids studied can form several structurally different secondary radicals.

Radicals $-CH_2-\dot{C}H-CH_2-$. As expected, the radicals in positions 4 and 12 in the phytane molecule have the same reactivity (the corresponding

product ratio is 1.05). However, these radicals positioned in the center of the molecules (positions 8) are slightly more reactive than similar radicals in positions 4: the reactivity ratios are 1.3 for pristane, 1.2 for phytane, and 1.7 for squalane. Reactivity of the secondary radical in position 12 of squalane is 2.4 times less than that of a similarly situated radical in position 8.

Radicals $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}-$. Reactivities of all radicals in positions 5, 7, 9, and 11 in the molecules are equal within $\pm 10\%$.

Relative reactivities of various secondary radicals. Significant differences between reactivities of differently flanked secondary radicals were found for all isoprenoids. Radicals $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$ are 4.8 times ($\pm 10\%$) more reactive than $\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}-$ radicals. The only exception was found for squalane: reactivity of the radical in position 12 is only 2.3 times higher than reactivity of the radical in position 11.

Primary radicals

Information on relative reactivity of primary radicals is limited due to difficulties in identification of the products of their β -scission and due to low content of the products. In the case of phytane the radical in position 6' has the same reactivity as the radical in position 14' and it is ca. 20% less reactive than the radical in position 10'.

The yields of scission products from the primary radicals in positions 1 are ca. 2 times less than those for the radicals in positions 6'. If one takes into account that only one scission route is available for the first radicals, it can be concluded that reactivities of all primary radicals in the isoprenoids are very close.

Comparisons of reactivities of various radicals

Comparisons of the yields of products from β -scissions of radicals of various structures allows approximate evaluation of their relative reactivities.

Primary radicals $\dot{\text{C}}\text{H}_2-\text{CH}-$ vs. secondary radicals $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$. The product ratio for scission of corresponding radicals for all isoprenoids is ca. 0.067. If one takes into account the differences between the numbers of C-H bonds in these groups, the ratios of reactivities of C-H bonds in the methyl group ($\text{CH}_3-\dot{\text{C}}\text{H}-$) and the central methylene group in the sequence $\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-\text{CH}(\text{CH}_3)$ is ca. 0.045 which corresponds to ΔE_{act} ca. -3.2 kcal/mol.

Primary radicals $\dot{\text{C}}\text{H}_2-\text{CH}-$ vs. secondary radicals $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}-$. The product ratio for scission of corresponding radicals for all isoprenoids is ca. 0.27 which translates into the difference between reactivities of corresponding C-H bonds ca. 0.18 and ΔE_{act} ca. -1.8 kcal/mol.

Secondary radicals vs. tertiary radicals $\text{CH}_2-\dot{\text{C}}(\text{CH}_3)-\text{CH}_2-$. The product ratio for scission of secondary radicals (in positions 8) and that for the tertiary radicals in positions 6 or 10 is 0.89. This corresponds to the ratio of ca. 2.25 for C-H bond reactivities in hydrogen abstraction reactions involving the tertiary $\text{CH}_3-\dot{\text{C}}\text{H}-$ groups and the central methylene groups in the isoprenoids (positions 8). Corresponding ΔE_{act} is ca. 0.8 kcal/mol. As was mentioned before, central CH_2 groups in $-\text{CH}_2-\text{CH}_2-\dot{\text{C}}\text{H}-$ sequences are less reactive than in $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ sequences. For them the corresponding C-H bond reactivity ratio is 11.6 and ΔE_{act} is ca. 2.6 kcal/mol.

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Table 1

ALKANES FORMED IN THERMOCRACKING REACTIONS OF PRISTANE, PHYTANE,
AND SQUALANE AT 250°C †

Alkane	Formed from			RRF (exp.)	RRF (calc.)	ΔRRF %
	Pristane (position of radical attack)	Phytane	Squalane			
n-C ₄		*(12)				
iso-C ₄	*(5)	*(5)	*(5)			
2-Me-C ₄	*(6)	*(6,11)	*(6)			
2-Me-C ₅	*(6',7)	*(6',7)	*(6',7)			
3-Me-C ₅		*(10)				
3-Me-C ₆		*(9,10')				
2-Me-C ₇	*(8)	*(8)	*(8)			
2,6-Me ₂ -C ₇	*(9)	*(9)	*(9)	-0.700	-0.700	0.0%
3-Me-C ₈		*(8)				
2,6-Me ₂ -C ₈	*(6)	*(7,10)	*(10)	-0.636	-0.644	1.2%
2,6-Me ₂ -C ₉	*(5,10')	*(10',11)	*(10',11)	-0.747	-0.736	-1.5%
3,7-Me ₂ -C ₉		*(6)		-0.578	-0.568	-1.7%
3,7-Me ₂ -C ₁₀		*(5,6')		-0.695	-0.674	-3.0%
2,6-Me ₂ -C ₁₁	*(4)	*(12)	*(12)	-0.833	-0.812	-2.5%
2,6,10-Me ₃ -C ₁₁	*(3)	*(13)	*(12)	-1.252	-1.175	-6.1%
3,7-Me ₂ -C ₁₂		*(4)		-0.788	-0.753	-4.5%
2,6,10-Me ₃ -C ₁₂	*(2,14)	*(3,14)	*(11)	-1.199	-1.114	-7.1%
2,6,10-Me ₃ -C ₁₃	*(1,2')	*(14',15)	*(10)	-1.353	-1.254	-7.3%
3,7,11-Me ₃ -C ₁₃		*(2)		-1.150	-1.076	-6.4%
2,6,10-Me ₃ -C ₁₃		*(9,10')		-1.430	-1.329	-7.1%
3,7,11-Me ₃ -C ₁₄		*(1)		-1.300	-1.210	-7.0%
2,6,10-Me ₃ -C ₁₅		*(16)		-1.477	-1.386	-6.2%
2,6,10-Me ₃ -C ₁₆			*(8)	-1.531	-1.407	-8.1%
2,6,10,15-Me ₄ -C ₁₆			*(7)	-1.940	-1.788	-7.9%
2,6,10,15-Me ₄ -C ₁₇			*(6)	-1.862	-1.705	-8.5%
2,6,10,15-Me ₄ -C ₁₈			*(5,6')	-2.102	-1.880	-10.6%
2,6,10,15-Me ₄ -C ₂₀			*(4)	-2.115	-2.063	-2.5%
2,6,10,15,19-Me ₅ -C ₂₀			*(3)	-2.345	-2.464	5.1%
2,6,10,15,19-Me ₅ -C ₂₁			*(2)	-2.320	-2.408	3.8%
2,6,10,15,19-Me ₅ -C ₂₂			*(1)	-2.455	-2.608	6.2%

† amounts of methane, ethane, and propane cannot be determined quantitatively and are not reported in the table.

Table 2

OLEFINS FORMED IN THERMOCRACKING REACTIONS OF PRISTANE, PHYTANE,
AND SQUALANE AT 250°C †

Olefin	Formed from			RRF (exp.)	RRF (calc.)	Δ RRF %
	Pristane (position of radical attack)	Phytane	Squalane			
C ₃ =	*(1)	*(1)	*(1)			
1-C ₄ =		*(14')				
2-C ₄ =		*(14')				
iso-C ₄ =	*(2)	*(2)	*(2)			
2-Me-1-C ₅ =		*(14)				
3-Me-1-C ₅ =	*(3)	*(3)	*(3)			
3-Me-1-C ₅ =		*(13)				
4-Me-1-C ₅ =	*(4)	*(4)	*(4)			
4-Me-1-C ₅ =		*(12)				
6-Me-1-C ₇ =	*(6')	*(6')	*(6')			
6-Me-2-C ₇ =	*(5)	*(5)	*(5)			
6-Me-1-C ₈ =		*(10')				
6-Me-2-C ₈ =		*(11)		-0.228		
2,6-Me ₂ -1-C ₉ =	*(6)	*(6)	*(6)	-0.520	-0.518	0.4%
2,6-Me ₂ -1-C ₉ =		*(10)		-0.455	-0.455	0.0%
3,7-Me ₂ -1-C ₉ =	*(7)	*(7)	*(7)	-0.896	-0.880	1.8%
3,7-Me ₂ -1-C ₉ =		*(9)			-0.803	
4,8-Me ₂ -1-C ₉ =	*(8)	*(8)	*(8)	-0.850	-0.846	0.5%
4,8-Me ₂ -1-C ₁₀ =		*(8)		-0.796	-0.785	1.4%
6,10-Me ₂ -1-C ₁₁ =	*(6')	*(6', 10')	*(10')	-0.915	-0.916	0.1%
6,10-Me ₂ -2-C ₁₁ =	*(7)	*(9)	*(9)	-0.799	-0.812	1.6%
6,10-Me ₂ -2-C ₁₁ =		*(7)		-0.751	-0.740	4.1%
2,6,10-Me ₃ -1-C ₁₁ =	*(6)	*(10)	*(10)	-1.047	-1.008	3.7%
3,7,11-Me ₃ -1-C ₁₂ =	*(5)	*(11)	*(11)	-1.459	-1.328	9.0%
2,6,10-Me ₃ -1-C ₁₂ =		*(6)		-0.992	-0.920	7.2%
4,8,12-Me ₃ -1-C ₁₃ =	*(4)	*(12)	*(12)	-1.436	-1.338	6.8%
3,7,11-Me ₃ -1-C ₁₃ =		*(5)		-1.398	-1.287	7.9%
4,8,12-Me ₃ -1-C ₁₄ =		*(4)		-1.379	-1.301	5.6%
5,9,13-Me ₃ -1-C ₁₄ =			*(12)	-1.505	-1.420	5.6%
6,10,14-Me ₃ -1-C ₁₅ =	*(1)	*(14')			-1.474	
6,10,14-Me ₃ -2-C ₁₅ =	*(3)	*(13)				
2,10,14-Me ₃ -5-C ₁₅ =	*(5)					
2,10,14-Me ₃ -6-C ₁₅ =	*(7)					
6,10,14-Me ₃ -1-C ₁₆ =		*(1)			-1.409	
6,10,14-Me ₃ -2-C ₁₆ =		*(3)			-1.326	
2,10,14-Me ₃ -5-C ₁₆ =		*(5)			-1.241	
2,10,14-Me ₃ -6-C ₁₆ =		*(7)			-1.241	
3,11,15-Me ₃ -6-C ₁₆ =		*(11)			-1.227	
3,11,15-Me ₃ -7-C ₁₆ =		*(9)			-1.227	
7,11,15-Me ₃ -1-C ₁₆ =			*(10')	-1.583	-1.494	5.6%
7,11,15-Me ₃ -2-C ₁₆ =		*(15)	*(11)	-1.530	-1.411	7.7%
7,11,15-Me ₃ -3-C ₁₆ =		*(13)				
2,6,10,14-Me ₄ -1-C ₁₇ =			*(14)		-1.525	
2,7,11,15-Me ₄ -1-C ₁₇ =			*(10)	-1.712	-1.562	8.8%
3,8,12,16-Me ₄ -1-C ₁₇ =			*(9)	-2.114	-1.909	9.7%
4,9,13,17-Me ₄ -1-C ₁₈ =			*(8)	-2.00	-1.963	2.0%
6,11,15,19-Me ₄ -1-C ₂₀ =			*(6')		-2.19	
6,11,15,19-Me ₄ -2-C ₂₀ =			*(7)		-2.13	
2,6,11,15,19-Me ₅ -2-C ₂₀ =			*(6)	-2.14	-2.18	1.9%

† olefins C₂₆-C₂₉ in the products of squalane thermocracking were not identified quantitatively and are not reported in the table.